



TITLE:

Research upon Joint Reaction and Transjointing. (III)

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Research upon Joint Reaction and Transjointing. (III)

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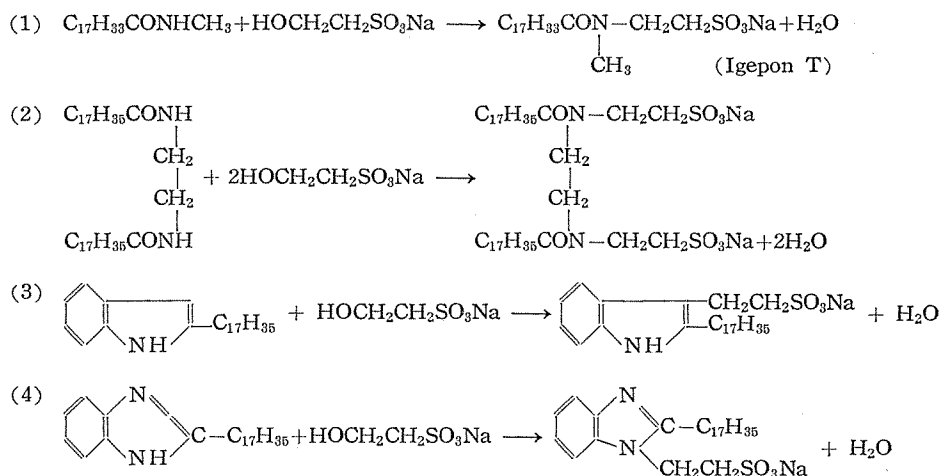
Continued from the previous report, the authors have performed the following researches upon Joint and Trans-jointing Reactions.

- (1) β -Sulfoethylation of some amides with sodium isethionate.
- (2) Joint Reaction of acid amides with orthoformate.
- (3) β -(2-Quinolino)-ethylation of some ketones.
- (4) Synthesis of *m*-aminomethyl-benzoic acid.
- (5) Transjointing Reactions with vinyl ether.
- (6) Transjointing Reactions with benzyl β -sulfo-ethyl ether.

Continued from the previous report¹⁾ the authors have performed the following investigations about the Joint Reaction and Transjointing.

Joint Reaction (A). Some β -Sulfoethylation Reactions

The β -sulfoethylations with sodium isethionate of N-methyloleamide, N,N'-distearoyl-ethylenediamine, 2-heptadecylindole and 2-heptadecylbenzimidazole were performed successfully.



The above four products are all anionic surface active agents. The reaction

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conditions and the yields of the above four experiments are given in Table 1.

Table 1. ^{a)}

Reaction component (g.)	Sodium isethionate (g.)	Temp.	Hr.	Yield ^{b)} g. (%)	Analysis of the products ^{c)}	
					N %	Na%
(1) 10	10	220°	13	3(20)	3.33 (3.50)	5.80 (5.75)
(2) 8	13	210°	11	2(17)	3.22 (3.38)	5.80 (5.55)
(3) 3	3	210°	12	1.5(33)	2.83 (2.96)	5.05 (4.86)
(4) 10	8	220°	9	4.0(30)	5.70 (5.92)	4.98 (4.86)

^{a)} In each case 0.3 g. powdered NaOH was added as the catalyser.

^{b)} The yields are the values for purified products.

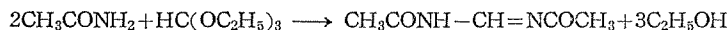
^{c)} The value given in the the parenthese are the calculated.

Joint Reaction (B), Joint Reaction of Acid Amides by Orthoformate

As already mentioned in the previous paper, the orthoformate joints two passive components in the following manner :

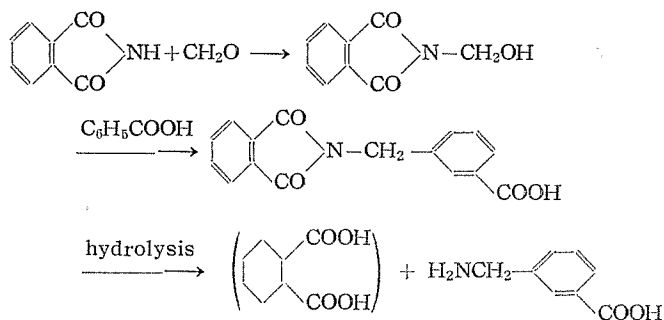


Recently C.W. Whitehead²⁾ has published an example of this Joint Reaction using urea as passive component. Only one simple example of this kind of Joint Reaction is known, in which acid amides were used as passive components.³⁾ The authors have confirmed that the following two Joint Reactions can occur.



Joint Reaction (C). Joint Reaction between Phthalimide and Benzoic Acid by Formaldehyde

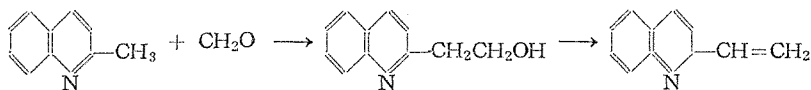
In order to obtain the *m*-carboxbenzylamine and its polycondensation product the following joint reaction was undertaken.



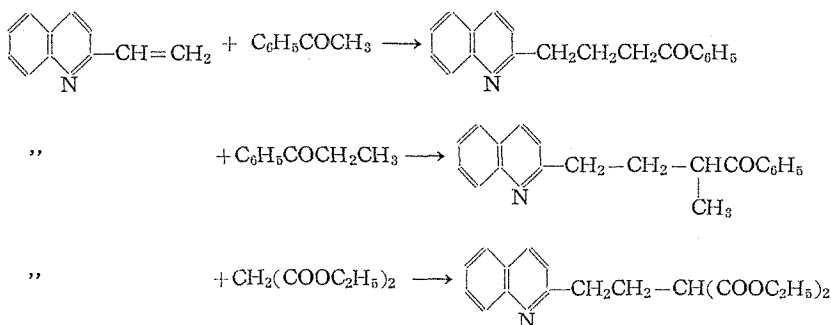
→ polycondensation (resin)

Joint Reaction (D). β -(2-Quinolino)ethylation

The 2-vinylquinoline was prepared by condensation quinaldine with formaldehyde and by dehydrating the 2-(β -oxyethyl)-quinoline.

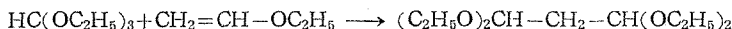
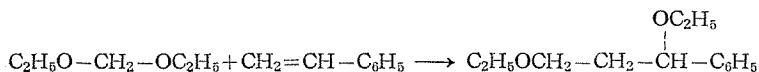
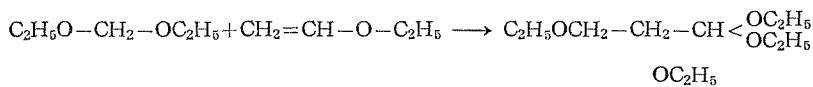


β -(2-Quinolino)-ethylation of some ketones and malonester with this 2-vinylquinoline was performed success-fully.



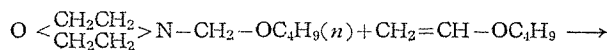
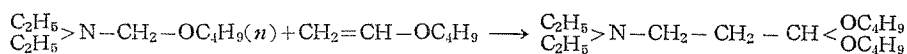
Transjointing (A). Transjointing between Formal and Vinylether

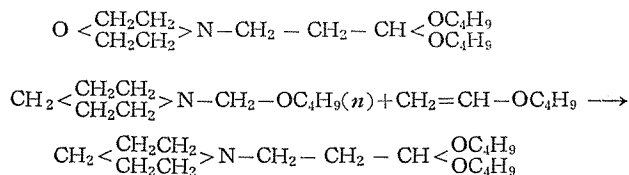
It is already known that the diethylformal and orthoformate react with vinyl-ether or styrene in the following manners using ZnCl_2 or BF_3 as catalyser.⁴⁾



As the diethylformal is a kind of jointed compound by formaldehyde, these reactions are typical Transjointing Reactions. At the same time these reactions are considered reasonably as an example of anionic Telomerization⁵⁾ and the above products are 1 : 1-Telomers respectively, except the case of styrene.

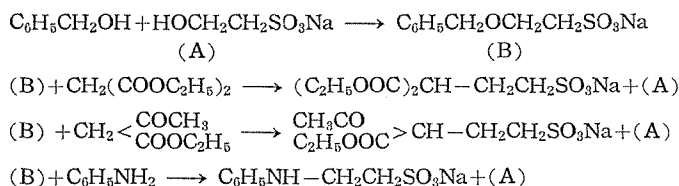
The authors considered that the analogous Transjointing would occur also with jointed compounds by formaldehyde other than formal and found this expectation as correct by confirming the following reactions experimentally.





Transjointing (B). Some Transjointing Reactions with β -Sulfoethylated Benzylalcohol

As already mentioned in the previous paper, alcohols can be sulfoethylated by sodium isethionate and this sulfoethylated compounds can be considered as a kind of jointed compound by formaldehyde. Therefore, Transjointing Reaction would be expected with this β -sulfoethylated alcohols. The authors have confirmed this Transjointing with β -sulfoethylated benzylalcohol, as shown in the following examples.



EXPERIMENTAL

Joint Reaction (A). β -Sulfoethylation with Sodium Isethionate

The melting point, iodine value and molecular weight of oleic acid, which was used for the experiment, were 12~12.5°C, 99 and 257. The melting point and molecular weight of stearic acid were 67~68° and 272. The N-methylethylamide was prepared from oleylchloride and methylamine (m.p.=32~33°) and the N,N'-distearoylethylenediamine was prepared from stearoylethylchloride and an excess of ethylenediamine (m.p.=145~146°). The 2-*n*-heptadecylindole was the same sample, which the authors had used for another purpose⁶⁾ (m.p.=68~69°) and the 2-*n*-heptadecylbenzimidazol was prepared from *o*-phenylenediamine and stearic acid after the method of Ralston⁷⁾ (m.p.=90~91°).

For the condensation given in the above Table, a three necked flask, equipped with a stirrer, thermometer and air condenser was used. The content was heated on an oil bath and when the temperature reached up to 180°, the catalyser, powdered NaOH, was added. In the case of N-methylethylamide the cooled reaction mass was washed with ether and the portion insoluble in ether extracted with hot alcohol and the hot alcoholic solution was evaporated after decolorization with carbon and the residue was then recrystallized from 90 % alcohol. In the case of N,N'-distearoylethylenediamine the reaction mass was extracted with boiling water and hot filtrated. The filtrate was evaporated and the residue was recrystallized

several times from 80 % alcohol. In the case of heptadecylindole and heptadecylbenzimidazole the reaction masses were treated with a small amount of hot alcohol and the residues were recrystallized several times from hot alcohol.

Joint Reaction (B). Joint Reaction of Acid Amides by Orthoformate

A mixture of 50 g. ethyl-orthoformate and 30 g. acetamide was refluxed for 15 hours. After cooling the separated solid was filtered, washed with acetone in order to remove the unreacted acetamide. The yield of the crude product was 23 ~27.7 % based on the acetamide. This was recrystallized three times from alcohol plus water (1 : 1). The product did not show a distinct melting point because of the decomposition. This product is insoluble in alcohol, acetone, benzene and ether and soluble in water and hot acetic acid.

N=22.16 % (calc. 21.86 %)

A mixture of 27 g. ethylorthoformate and 12 g. benzamide was refluxed for 12 hours and the reaction mass was treated as above. The crude yield was 8.2 g. After recrystallization from ethanol the product showed a melting point of 207~208°.

N=11.39 % (calc. 11.11 %)

Joint Reaction (C). Joint Reaction between Phthalimide and Benzoic Acid by Formaldehyde

The N-methylolphthalimide was prepared as the usual method. A 0.1 mole sample of N-methylolphthalimide and 0.1 mole benzoic acid was dissolved in 100 cc of 95 % H_2SO_4 and stood for four days at 10-15°C. The reaction mass was poured into ice water. The white precipitate was filtered and extracted with soda solution. The soda solution was acidified with HCl and the aimed *m*-phthalimidomethyl-benzoic acid was obtained in crude state, the yield was ca. 17 g. This product was recrystallized from alcohol.

m.p.=228.5-230.5°, N=5.36 % (calc. 4.98 %)

Next, this *m*-phthalimidomethyl-benzoic acid was hydrolyzed by refluxing in 20% NaOH solution. On acidifying with HCl separated out the phthalic acid, which was removed by filtration and the filtrate was evaporated to dryness. This crude hydrochloric acid salt of *m*-aminomethyl-benzoic acid was recrystallized from absolute alcohol. The yield was 88.5 %. m.p., 250-251°C.

Found : C, 51.45 ; H, 5.48 ; N, 7.36. Calcd. for
 $\text{C}_8\text{H}_{10}\text{O}_2\text{NCl}$: C, 51.21 ; H, 5.37 ; N, 7.47.

In order to obtain the free aminomethyl-benzoic acid from the above hydrochloric acid salt, the latter was dissolved in water and passed through a column, packed with Amberlite IR-4B, after the method of Org. Synth⁹⁾. The elute was evaporated. The yield was 88 % of the theory, m.p., 246-248°C.

Upon heating this free aminomethylbenzoic acid at 245-255°C for five hours a

brittle and hard resin was obtained.

Joint Reaction (D). β -(2-Quinolino)-ethylation

Quinaldine (50g.) was dissolved in a mixture of 25 cc. water and 27 cc. ethanol to this solution 1.5 equivalent amount of formaldehyde as 37 % solution was added and refluxed for 24 hours. The solvent was removed by distillation under vacuum and the residual 2-oxyethylquinoline was next dehydrate into 2-vinylquinoline by distilling together with 1.3 g. solid NaOH and 0.5 g. N-phenyl- β -naphthylamine (as polymerization inhibitor). The crude distillate was redistilled, b.p. = 120-127°/7-8 mm. The yield was only 7 %.

To a mixture of 3.5 g. of the above 2-vinylquinoline and 13.4 g. propiophenone (1 : 2 mole ratio) 0.11 g. metallic sodium was added and heated at 160-170° for 6 hours, the reaction mass was distilled and the following fractions were obtained.

1. 68-73°/0.8 mm, 0.3 g ;
2. 185-193°/0.9 mm, 1 g ;
3. 193-200°/0.9 mm, 2.6 g.

From the fraction 3 the 2,4-dinitrophenylhydrazone of the aimed product was separated, purified and analyzed.

Found : C, 66.54 ; H, 5.10 ; N, 15.21.

Calcd. for $C_{26}H_{28}N_{604}$: C, 66.52 ; H, 4.90 ; N, 14.93.

A sample of 3.1 g. 2-vinylquinoline was dissolved in a small amount of ethanol and added to a absolute alcoholic solution, which contains 16 g. diethyl malonate and 0.46 g. sodium ethylate and refluxed for 5 hours. The reaction solution was fractionated and a fraction boiling at 180-190°/0.7-0.8 mm. was caught (ca. 1.5 g.). This product was converted into its picrate and recrystallized from alcohol, m.p. 92-94°.


Found : N, 10.05.

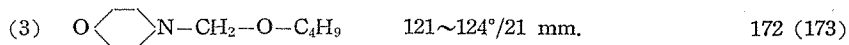
Calcd. for $C_{22}H_{24}O_{11}N_4$: N, 10.29.

This product was saponified and HCl-salt of γ -(2-quinolino)-butyric acid was obtained in 66 % yield. m.p., 165-168°.

Transjointing (A). Transjointing Reaction with Vinyl Ether

The vinylether, which was used for experiment, was the vinyl *n*-butyl ether. This was dried with anhydrous Na_2SO_4 and the fraction, boiling at 92-95°, was collected. The dialkylaminomethyl *n*-butyl ethers were prepared after the method of T.D. Stewart⁹⁾. As the dialkylamine piperidine, diethylamine and morpholine were used and the boiling points and neutralization values of the dialky-aminothyl *n*-butyl ethers are as follows :

	b. p	Neutralization value
(1)  N-CH ₂ -O-C ₄ H ₉	110-113°/24 mm.	176 (171)
(2) (C ₂ H ₅) ₂ N-CH ₂ -O-C ₄ H ₉	171-173°/760 mm.	157 (159)



The neutralization values were measured by titrating the alcoholic solutions of each ether with 0.2*N* HCl using methylorange as indicator. The values in the parentheses are the calculated.

The Transjointing Reaction between these dialkylaminomethyl butyl ether and vinyl butyl ether was at first undertaken without any catalyser, but no reaction took place. Therefore the *p*-toluene-sulfonic acid was chosen as a catalyser, i.e., 0.02 g. *p*-toluene-sulfonic acid was added to a mixture of 0.1 mole of both components and this mixture was heated for 10 hours at 98°. The reaction solution became gradually brownish. After neutralizing the catalyser with K₂CO₃, the reaction solution was fractionated and the following results were obtained.

	Pre-fraction (g.)	Chief-fraction	Yield g. (%)	Residue (g.)
(1)	5	154-155°/5.5 mm.	19.5 (72)	1.0
(2)	4	122-123°/4.5 mm.	15.5 (60)	1.0
(3)	4.2	155-157°/5 mm.	21.0 (77)	0.5

The chief-fractions were all colorless and basic liquid and the neutralization values of these chief-fractions were measured and found as follows :

- (1) 264 (calcd. for C₁₆H₃₃NO₂ 271)
- (2) 253 (calcd. for C₁₅H₃₃NO₂ 259)
- (3) 268 (calcd. for C₁₅H₃₁NO₃ 273)

Next each chief-fraction was submitted to hydrolysis to the corresponding free aldehydes, treating with HCl or oxalic acid, but viscous basic oils were obtained in each case. For example 6 g. of dibutylacetal of β -piperidino-propionaldehyde was added to 25 cc. conc. HCl, cooling externally. A white crystalline product precipitated temporarily, but disappeared soon again. After standing overnight, the mixture was distilled in vacuo. Water and butanol (ca. 2.5 g.) distilled out. The residue was washed with Na₂CO₃. An oily product separated out. This was extracted with ether and after evaporating the ether a viscous, yellow oil was obtained. This oil exhibits silver-mirrors reaction, red color with Schiff's solution and has a neutralization value 136. From these facts it can be concluded that this oily product is a polymerized aminoaldehyde. As already mentioned, a white crystalline precipitate is produced by treating the original aminoaldehyde-acetal with HCl. This was carefully collected, i.e. the aminoaldehyde-acetal was dissolved in ether, dry HCl-gas was introduced into this solution and the white precipitate was filtered quickly. This was dissolved in alcohol, reprecipitated with ether and dried, m.p., 133-136°.

The neutralization value and the C,H-analysis are as follows and coincide pretty good with the calculated values as the hydrochloric acid salt of the dibutylacetal

of β -piperidino-propionaldehyde.

	Neutralization value	C	H
Found.	302	62.74 %	10.94 %
Calcd. for $C_{16}H_{34}NO_2Cl$	307.5	62.54 %	11.07 %

Further, the 2,4-dinitrophenylhydrazone of this β -piperidino-propionaldehyde was obtained directly from its dibutylacetal, i.e. 2 g. 2,4-dinitrophenylhydrazine was dissolved in 24 cc. H_3PO_4 (80 %); to this solution 2 g. of the dibutylacetal was added and heated on a water bath for one hour. After standing 2 days, the solution was neutralized with Na_2CO_3 -solution and brownish crude hydrazone precipitated. This was redissolved in absolute alcohol and precipitated again with phosphoric acid. After recrystallization five times from alcohol it was analyzed. The found values coincide good with the calculated.

	C (%)	H (%)	N (%)
Found :	40.50	5.24	16.68
Calcd. for $C_{14}H_{22}N_5O_8P$:	40.00	5.24	16.67

This phosphoric acid salt of the hydrazone was made free by treating with Na_2CO_3 -solution and analyzed again.

	C (%)	H (%)	N (%)
Found :	53.02	5.99	21.39
Calcd. for $C_{14}H_{19}N_5O_4$:	52.34	5.92	21.81

From these facts and values it is obvious that the expected Transjointing Reaction has doubtlessly occurred between the dialkylaminomethyl butyl ethers and vinyl butyl ether.

Transjointing (B). Transjointing Reaction with Benzyl β -Sulfoethyl Ether

Synthesis of benzyl β -sulfoethyl ether. In a threenecked flask, equipped with stirrer, thermomater and reflux condenser, a mixture of 150 g. benzyl alcohol and 45 g. sodium isethionate was heated up to 180°C. At this temperature the isethionate dissolved in benzylalcohol and then 1.5 g. powdered NaOH was added. A yellowish solid separated out once, but it disappeared again. After heating for 7 hours at 180-190°, the content was cooled and powdered. The powdered product was washed with ether and the insoluble residue was recrystallized from 90 % ethanol. The yield was about 50 g. (70 % of theory).

Transjointing with malonic ester. In a three-necked flask, equipped with stirrer, thermometer and reflux condenser, 1.3 g. metallic sodium was dissolved in 50 cc. absolute alcohol and 100 g. diethyl malonate was then added. After the removal of the solvent, 11 g. benzyl- β -sulfoethylether was added and heated at 170° for 20 hours. After cooling the reaction mass was washed with ether and the

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portion insoluble in ether was extracted with water. This aqueous solution was neutralized with hydrochloric acid and was evaporated to dryness and the product was recrystallized several times from alcohol.

Yield : 3.7 g (25 %)

Found Na : 8.14, Calcd. for $C_9H_{15}O_7SNa$ 7.93.

The Transjointing with acetoacetic ester was performed similarly to the above.

Yield : 3 g. (20 %)

Found Na : 8.95. Calcd. for $C_8H_{13}O_6SNa$ 8.84.

The Transjointing with aniline was performed by heating the mixture at 180° for 14 hours, using powdered NaOH (1 g.) as a catalyser. The product was washed with ether and then recrystallized several times from alcohol.

Yield : 2 g. (22 %)

Found : N, 6.11. ; Na, 10.55. Calcd. for $C_8H_{10}O_5NSNa$ N. 6.28. ; Na, 10.31.

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